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Blue Phase Templating

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Materials with nanoscale features are of increasing interest in a wide range of technological applications. New fabrication techniques are often required as the length-scale is reduced and conventional methods meet their fundamental limits; of particular utility is molecular self-assembly, in which structure emerges spontaneously. A promising approach to the self-assembled formation of novel materials is the transfer of liquid-crystalline structure to polymers [1]. Here we report on the application of this concept to Blue Phase I, a chiral liquid crystal with cubic symmetry [2]. Blue Phase I was photopolymerized and the remaining liquid crystal removed, creating a porous free-standing cast which retains the three-dimensional structure of the blue phase. The cast may, in turn, be used as a hard template for the formation of new materials. The fabrication process is shown in Fig. 1.

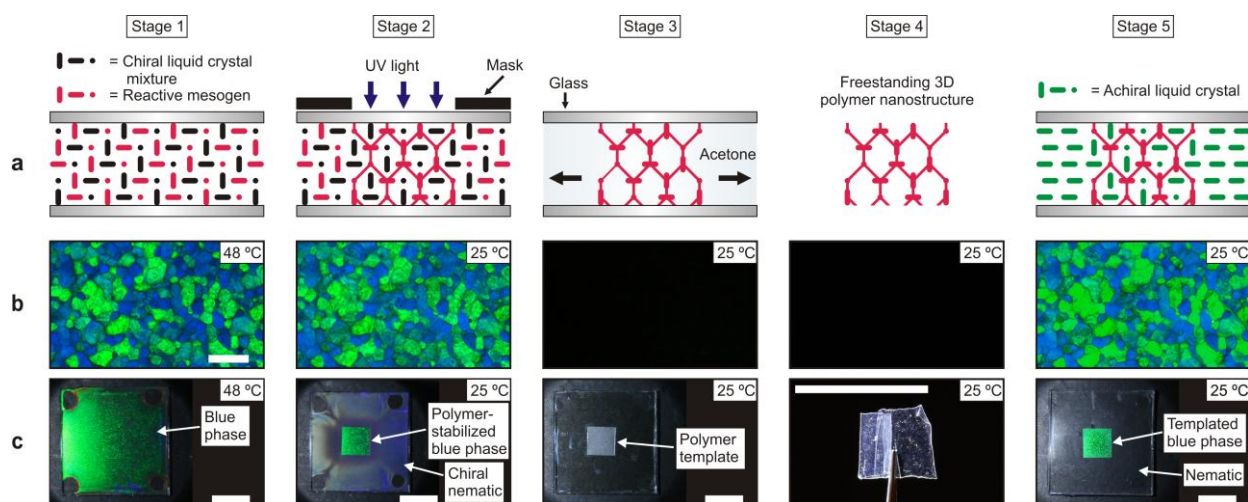


Figure 1. Formation of the 3D nanostructured polymer. **a**, Schematic diagram of the procedure. **b**, Transmission optical polarizing microscopy images (100 μm scale bar). **c**, Photographs of cell (5 mm scale bars). Stage 1: a blue phase self-assembles between two glass sheets. Stage 2: the cell is exposed to ultraviolet light with a square-aperture mask to photopolymerize the reactive mesogen. Upon cooling to room temperature, the exposed region is observed to be stabilised in the blue phase, while the unexposed regions transition to the chiral nematic phase. Stage 3: the cell is placed in acetone to wash out the liquid crystal, chiral dopant, and the remaining photoreactive mesogen. The remaining polymer structure is effectively non-transmissive between crossed polarizers. Stage 4: the solid polymer structure may be removed from the cell. Stage 5: an unopened cell is refilled with an achiral nematic liquid crystal. There are no chiral molecules included as additives, yet a blue-phase-like structure is observed in the polymer templated regions.

By refilling the cast with the wide-temperature-range achiral nematic material BL006 (Merck), we created templated blue phases which are shown to have unprecedented thermal stability (over a 250 $^{\circ}\text{C}$ range) when compared to conventional systems (0.5–2 $^{\circ}\text{C}$ range), to bimesogenic systems (40 $^{\circ}\text{C}$ range [3,4]), or to the polymer-stabilised systems of Kikuchi *et al.* (60 $^{\circ}\text{C}$ range [5]): see Fig. 2.

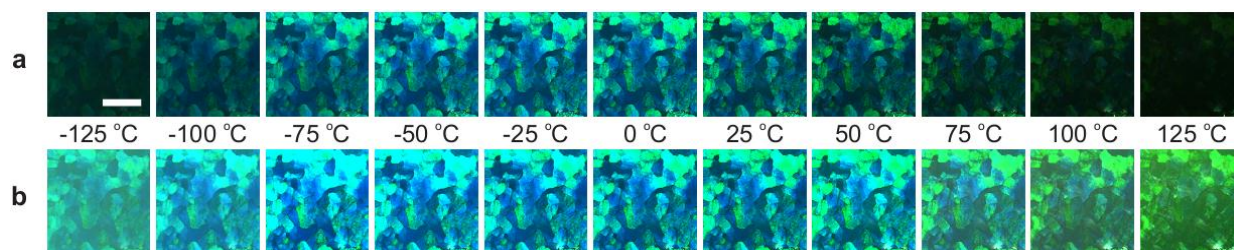


Figure 2. **Thermal stability of the templated blue phase.** Polarizing optical microscope images indicate the range of thermal stability (100 μm scale bar). **a**, Images with equal illumination indicate gradual loss of birefringence at low and high temperatures. **b**, Intensity enhanced images clarify that the structure persists over a range of at least 250 $^{\circ}\text{C}$, from -125 $^{\circ}\text{C}$ to 125 $^{\circ}\text{C}$.

In addition, we demonstrate that the templated blue phase can act as a mirrorless laser and an electro-optic phase device. Thus, this new method for the self-assembled fabrication of 3D nanostructures may be of use in diverse applications.

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